BARRIER, THERMAL AND MECHANICAL PROPERTIES OF POLYURETHANE-MODIFIED CLAY NANOCOMPOSITES FOR THERMAL INSULATION MATERIAL

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ABSTRACT

In this thesis, the effect of modification through transition metal ions (TMI) on montmorillonite (MMT) clay that was incorporated into thermoplastic polyurethane (PU) was discussed. The TMI modification was intended to achieve a good dispersion of the clay into PU with fewer agglomerates. The modification of the MMT clay was carried out using Copper (II) Chloride and Iron (III) Chloride. The fabrication of the nanocomposites was done via solution intercalation method by employing chloroform as the solvent. The clay content was varied at three different clay loadings (1 to 3 weight percentage). The existences of the TMIs on the modified clay were confirmed through Inductive Couple Plasma Mass Spectrometry (ICP-MS) whereas its morphological structure was tested through Field Emission Scanning Electron Microscope (FESEM) and X-Ray Diffraction (XRD). The morphology of PU-MMT nanocomposites was determined through Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), XRD and FESEM. The mechanical properties of the nanocomposites were studied through its tensile stress and elongation at break whereas its thermal properties were analysed using Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and thermal conduction. Gas and water permeation through the nanocomposites was employed to investigate the nanocomposite's barrier properties. The modification process was proved successful as high amount of copper and iron ions were detected in the ICP-MS and even distribution of the clay was obtained in FESEM. XRD data with higher d-spacing values was obtained for PU with modified clay which suggests that a good intercalated structure has been achieved. SEM micrographs illustrated lesser agglomerates in PU with modified clay nanocomposites due to the TMI modification that enables an even distribution of the clay into PU. The homogeneous dispersion of the clay strengthened the structure of PU which led to a remarkable improvement in its mechanical properties. The highest increase in tensile stress was obtained in 2% PU-MMT Cu which showed 148% hike in its 1% and 3% clay loading. The thermal stability was also improved in the modified nanocomposites due to its higher thermal degradation temperature however there were no significant effect of the clay on the melting temperature of the nanocomposites. Thermal conductivity of the PU nanocomposites decreased with increasing clay loading which makes it a suitable thermal insulation material. Both the gas and water permeability decreased in PU with modified clay nanocomposites due to the formation of the tortuous path in its matrix. The highest significant decrease in the gas permeation analysis amounted to 68% in 3% PU-MMT Fe and 40 times decrement in water permeation coefficients were obtianed in 1% PU-MMT Fe. The results obtained showed that the incorporation of modified clay into PU has brought significant improvements in its properties.

ABSTRAK

Dalam tesis ini, kesan pengubahsuaian melalui ion logam peralihan (TMI) pada montmorillonit (MMT) yang telah dimasukkan ke dalam poliuretana termoplastik (PU) telah dibincangkan. Pengubahsuaian TMI bertujuan untuk mencapai penyerakan MMT yang menyeluruh ke dalam PU. Pengubahsuaian MMT telah dijalankan dengan menggunakan kuprum (II) klorida dan ferum (III) klorida. Fabrikasi nanokomposit telah dilakukan melalui kaedah interkalasi dengan menggunakan kloroform sebagai pelarut. Kandungan MMT telah diubah dalam tiga jenis pembebanan yang berbeza (1 hingga 3 peratus). Kewujudan TMIs di struktur MMT yang diubah suai telah disahkan melalui Induktif Plasma Mass Spektrometri (ICP-MS) manakala struktur morfologinya telah diuji melalui Mikroskop Imbasan Elektron (FESEM) dan X -Ray Belauan (XRD). Morfologi nanokomposit PU-MMT telah ditentukan melalui Spektroskopi inframerah transformasi Fourier (FTIR), Mikroskop Imbasan Elektron (SEM), XRD dan FESEM . Sifat-sifat mekanik nanokomposit telah dikaji melalui tekanan tegangan dan pemanjangan pada takat putus manakala sifat haba dianalisis dengan menggunakan analisis Termogravimetri (TGA), Kalorimeter Pengimbasan Perbezaan (DSC) dan pengaliran haba. Resapan gas dan air melalui nanokomposit telah digunakan untuk menyiasat ciri-ciri kebolehtelapan nanokomposit ini. Proses pengubahsuaian telah terbukti berjaya apabila jumlah kuprum dan ferum yang tinggi dikesan di ICP-MS dan juga penyerakan MMT yang homogen telah diperoleh dalam FESEM . Data XRD dengan nilai-nilai d-jarak yang lebih tinggi telah diperolehi bagi PU- MMT yang diubahsuai menunjukkan bahawa struktur interkalasi yang baik yang telah dicapai. Analisis SEM menunjukkan pengelompokan yang kurang di dalam PU-MMT nanokomposit diubahsuai kerana pengubahsuaian TMI telah membolehkan penyerakan MMT yang lebih teratur ke dalam PU. Komposisi MMT yang lebih homogen telah memantapkan struktur PU yang membawa kepada peningkatan luar biasa dalam sifat mekanikalnya. Peningkatan tertinggi sebanyak 148% dapat dilihat dalam tegasan tegangan pada 1% dan 3% muatan MMT di dalam 2% PU-MMT Cu. Kestabilan haba juga telah bertambah baik pada nanokomposit yang diubah suai disebabkan oleh suhu degradasi haba yang lebih tinggi berbanding sampel lain, walaubagaimanapun tidak ada kesan yang ketara pada suhu lebur nanokomposit . Kekonduksian terma daripada nanokomposit PU menurun dengan bebanan MMT yang tinggi di mana ini dapat menjadikan ia sebagai bahan penebat haba yang sesuai. Kedua-dua kebolehtelapan gas dan air menurun dalam PU nanokomposit yang diubahsuai kerana pembentukan laluan rumit dalam matriks itu. Penurunan yang tertinggi dalam analisis resapan gas berjumlah 68% didapati dalam 3% PU-MMT Fe . Keputusan yang diperolehi menunjukkan bahawa serakan tanah liat diubahsuai ke dalam PU telah membawa peningkatan besar yang ketara dalam sifat-sifatnya.

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LIST OF SYMBOLS

λ	Wavelength
θ	Angle
^{o}C	Degree Celcius
ε	Elongation
%	Percentage
J_{st}	Flux
a	Water activity
T_d	Degradation temperature
T_{pm}	Melting temperature peak
q	Heat Flow
t	Interface Thickness
A	Area
Δ	difference

LIST OF ABBREVIATIONS

PU	Polyurethane
HS	Hard Segment
SS	Soft Segment
MMT	Montmorillonite
PLSN	Polymer layered silicate nanocomposites
PNC	Polymer nanocomposites
TMI	Transition Metal Ions
Cu	Copper
Fe	Iron
LS	Layered silicates
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
FESEM	Field Emission Scanning Electron Microscope
TGA	Thermal Gravimetric Analysis
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The development of polymer clay nanocomposites began as early as 1930s by a MIT professor, E.A. Hauser who worked on latex systems. The evolution of the technology was continued by Jordan and colleagues, who produced highly dispersible organo bentonites in 1940s, however the field only began to gain wide attention with a research progressed by Toyota Motor Co when they reported unusual property improvements in nylon-6/montmorillonite nanocomposites (Kim et al., 2003). Resurgence in interest in polymer nanocomposites has then started to begin due to the property improvements. Polymer nanocomposites consist of a filler reinforcement material, usually found in a nanometer scale size dispersed in a polymer matrix and often this reinforcement creates a new class of polymer composite with improved physical and functional properties (Usuki et al., 2005). The fillers can be one dimensional; nanotubes and fibers, two dimensional; clay and graphite or three dimensional; spherical particles (Ray and Bousmina, 2006). It can be noted in general that polymer nanocomposites exhibit improved polymer properties and their use may invent certain new properties that cannot be derived from its pristine state (Hussain et al., 2006).

The synthesis of polymer nanocomposites is seen as a great scientific and industrial importance due to their improved properties. The synthesis of polymer nanocomposites such as polymer/clay nanocomposites (PCN) is seen as an opportunity to tailor its properties for a wide range of applications and has expanded into most of the engineering polymers such as polycarbonate, polyurethane, polystyrene, polyvinylchloride and polylactide. A review by Reddy (2011) reported that currently the application of polymer nanocomposites in the engineering world has become state of the art due to the improved mechanical, thermal, conductivity and barrier properties of the polymer composites. The enhancement in properties of the polymer is obtained through the complete exfoliation of the fillers in its polymer matrix and amongst the many types of fillers available, clay minerals are usually the preferred choice as a filler as it is naturally abundant, environmentally friendly, chemically stable and inexpensive (Tjong, 2006).

The improvement in the mechanical properties was first reported by Wang and Pinnavaia (1998) whom reported a more than 100% increase in modulus, strength and extensibility in PCN. Improvements in mechanical properties of nylon 6-clay nanocomposites were also reported by Fornes et al. (2002) whereby they obtained a twofold increase in the Young's modulus with an addition of 3 wt% clay. Hasegawa et al. (2003) also reported a hike of 28% and 14% in tensile and flexural moduli with the incorporation of only 1.6 wt% clay. Polymer nanocomposites have also been reported to portray excellent enhancements in its thermal properties. According to a study conducted by Usuki et al. (1993), a loading of 4.2 wt% clay showed an increase of 80^{o}C in the heat distortion temperature of nylon 6–clay nanocomposite compared to the pristine polymer. According to Saha et al. (2008), the decomposition of nanophased polyurethane foams shifted to a high temperature with the infusion of nanoparticles. This proves that the incorporation of nanoparticles into the foam offers a stabilizing effect against decomposition and creates protection against thermal degradation.

Apart from the improvements in the mechanical and thermal behavior, remarkable advancement was also seen in the barrier properties of polymer nanocomposites. The platelet structure of the layered silicates is seen to improve the barrier properties according to a tortuous path model whereby great significance in reducing the diffusivity of gases through nanocomposites are seen with only small addition of platelet particles. Yano et al. (1997) investigated in their study and found that at 2 wt% of clay, the relative permeability coefficient of polyamide-clay hybrid films decreases. Apart from that, in a study by Osman et al. (2003), the oxygen transmission rate asymptotically decreased with increasing aluminosilicate volume fraction whereby 30% reduction was achieved at 3 vol%.

The field of polymer composites has been expanded into almost all types of polymer. One of the most versatile polymers that are being researched is polyurethane (PU) due to its wide usage in many fields such as in coatings, composites, roofing materials and as adhesives, however pristine PU is seen to possess insufficient physical and functional properties to accommodate these applications. The incorporation of clay into a polymer could improve its properties according to the desired applications (Wang et al., 2008 and Liu et al., 2006) and the same is applicable to PU. Recently, the application of PU as a thermal insulator was seen to be in the lime light due to the high demand of energy conservation and the importance of heat management. The heat absorption capacity, chemical stability and the ability to form sandwich structures with various facer materials makes PU as a preferred thermal insulation material choice (Demharter, 1998).

Lately, the use of clay based materials as reinforcement fillers for polymers has attracted much scrutiny. There are various techniques applied in preparing the PCNs such as melt intercalation, *in situ* polymerization, and solution intercalation method. It is important to ensure that the techniques applied are suitable with the polymeric material used. This study describes the synthesis of polyurethane/montmorillonite clay nanocomposites (PU-MMT) using solution intercalation technique. Layered silicates (LS) have attained much attention in the past because they can be dispersed in a polymer matrix at the nanometer scale to yield reinforced PCN (Usuki et al., 1993) however the modification of clay is seen as an essential requirement. Several authors such as Singla et al. (2012) and Nawani et al. (2007) have reported the usage of organic cations to modify clay for the preparation of PCNs. As part of this study, the use of transition metal ions (TMI) as a modifier for the montmorillonite clay was studied.

The TMI modification was carried out to change the nature of the clay which is hydrophilic as this particular nature creates poor mixing and interaction with most polymer matrices that are hydrophobic (Olphen, 1977, Giannelis, 1996). Apart from that, the structure of the layered silicate consists of stacks that are held tightly by electrostatic forces and it is crucial for the clay to undergo modification before the preparation of nanocomposites to exfoliate it into single layers. Clay that is not modified would not be effective as it will not be able to interact with the polymer matrix (Singla, 2012). Naturally occurring LS consists of cations that are not strongly bound to the clay surface and transition metal ions (TMI) are used to exchange the cations present in the clay. This process helps to separate the clay platelets in order for them to be more easily intercalated or exfoliated, and also enables the clay to be more compatible with a wide range of polymer matrix. The TMIs that were chosen in this work was copper (Cu) and iron (Fe) ions due to their catalytic performance. Previous work on polymer clay nanocomposites using organic modifiers were reported by Xie et al. (2001), Davis et al. (2002), and Huskic et al. (2013) whereby all authors reported significant improvement in the nanocomposites properties.

1.2 PROBLEM STATEMENT

The study of polyurethane composites has acquired great importance due to its wide applications. One of the most important applications of PU is as a thermal insulation material, however, there are certain drawbacks that need to be rectified in order for it to be durable and effective. In this work, PU is studied as a thermal insulation material. It is important for an insulation material to have good mechanical protections, barrier protections, and its main requirement is that it possesses low thermal conductivity. Generally, an intrinsic property of a thermal insulation material is that it has a porous structure and this porosity allows conduction through it due to the air contained in the small pores (Roymech, 2013).

Jiawen et al. (2004) reported in their study that PU has poor thermal stability and poor barrier properties. The barrier properties of PU are meager as compared to other polymers (Osman et al., 2003) due to its porous structure which enables easy transportation of gases and water. They also stated that this may contribute to the poor conduction property of PU. Apart from that, PU has also been reported to possess poor high temperature capabilities due to it's a restriction by an upper temperature capability of approximately 175^{o}C and if exposed to higher temperature, it has a tendency to soften and lose its strength (Elder Rubber Company, 2013). Furthermore, PU is also known to have a low sustainability to direct sunlight. It is important for a thermal insulation material to meet certain characteristics such as low thermal conductivity and it also crucial for these materials to be able to maintain it even when they are perforated by external force or objects.

The incorporation of layered silicates into PU often creates a nonhomogeneous dispersion due to the clay's interlayer Van der Waals forces which creates clay agglomerates. The clay agglomerate that appears in the structure of the nanocomposites hinders the property advancement of the polymer thus it is also very important to ensure that the dispersion of the clay platelets into its matrix is achieved successfully.

1.3 RESEARCH OBJECTIVES

The objectives of this study were the following:

1. Investigated the use of solution intercalation method for the preparation of polyurethane nanocomposite using pristine and modified Na^{+} montmorillonite clay.

2. Modified the conventionally obtained montmorillonite clay (MMT) by two types of transition metal ions which are Cu^{2+} ions and Fe^{3+} ions.

3. Investigated the mechanical properties, thermal properties and permeability properties of polyurethane nanocomposites films containing the pristine and modified clay and comparing these properties to the neat properties of the polymer.

1.4 SCOPE OF STUDY

A general scope or an experimental framework of this thesis was established by underlining the steps taken to achieve the objectives of the proposed research. Following are the designed scopes that were seen as a guidance and assistance in achieving the research objectives of this work.

1. The preparation of PU-MMT nanocomposites was achieved through solution intercalation method due to the better mixing performance and to avoid the degradation of the PU's structure. The morphology of the obtained nanocomposites lattices and their films will be characterized to investigate whether the synthesis created an intercalated or exfoliated morphology.

2. The modification of the MMT clay was carried out through the transition metal ions which were copper (II) chloride and iron (III) chloride ions. The characterization of the modified clay was executed using inductively coupled plasma mass spectrometry (ICP-MS), x-ray diffraction (XRD) and Field Scanning Electron Microscope (FESEM). During the preparation of PU-MMT nanocomposites, a series of clay content (from 1% to 3%) are varied.

3. The structure of PU-MMT is characterized using (XRD) and visually interpreted through the application of scanning electron microscopy (SEM) and FESEM. The thermal stability of the PU-MMT samples is investigated by using thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC) and thermal conductivity. The mechanical study of the PU-MMT nanocomposites are carried out via Universal Testing Machine whereby the data obtained for its tensile stress and the elongation at break is analyzed. The permeability analyses of the samples were employed through the membrane separation unit for the gases and water permeability unit.

1.5 SIGNIFICANCE OF RESEARCH

In this research, it was aimed to obtain well dispersed clay into PU to minimize the clay agglomerations and hinder the deterioration of the nanocomposites properties. In order to aid this effort, transition metal ions modification was done on the clay to create a good compatibility with PU and to ensure that a homogeneous dispersion of the clay has been achieved, the preparation of PU-MMT nanocomposite should be executed under certain processing conditions. Solution intercalation was employed in preparing the PU-MMT in order to reduce the risk of thermal degradation as PU is known to have a low melting temperature due to the low glass transition temperature of polyol which is less than 70^{o}C (Rlhudson, 2011).

The study of polymer nanocomposites is an interesting topic which has been studied extensively however to the best of the authors knowledge, there are no reports to date that studied the properties of PU with clay modified with transition metal ions. Although there are reports on the improved properties using MMT clay, the clay used are modified by the supplier and is often classified as Cloisite 10A, 15A, 20A and 30B. In this work, the MMT clay was modified using copper and iron ions before it was incorporated into PU. Properties of the nanocomposites that were studied include mechanical, thermal and barrier. It is to be noted that there are no previous work on the gas and water barrier properties of polyurethane with TMI modified clay nanocomposites. It is presumed that the incorporation of organically modified clay will be able to generate a new class of nanocomposites with improved properties.

This study is to aid industries that are based on insulation materials such as roofing industry. It is anticipated that the PU-MMT will serve as a good insulation material by creating a good heat shield and temperature the environmental temperature variations. According to Stockton (2011), it is also important for the material to withstand the ravages of sun, rain and leakages thus it is expected that the advancement in the thermal, mechanical and barrier properties of this nanocomposites will accommodate to the necessary needs that are required for an insulation material.